

# Miniemulsion and Conventional Emulsion Copolymerization of Styrene and Butadiene: A Comparative Kinetic Study

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**ABSTRACT:** The kinetics of conventional and miniemulsion copolymerizations of styrene and butadiene were compared using the Mettler RC1 calorimeter. A two-step homogenization procedure was applied to obtain miniemulsions of these monomers with hexadecane as the costabilizer. The results indicated that the miniemulsion polymerizations proceeded mainly by nucleation in the monomer droplets, while in the conventional emulsion polymerizations, particle formation occurred by a combination of micellar and homogeneous nucleation. The overall rate of miniemulsion polymerization was faster than the corresponding conventional emulsion system if the surfactant concentration was below the critical micelle concentration

(cmc) and slower if the surfactant concentration was above the cmc. The homogenization process is important for making stable miniemulsion systems, but had no effect on the conventional emulsion system (without hexadecane), most likely because of the second stage addition of the butadiene monomer. The dependencies of the rate of polymerization (heat of reaction) and number of particles on the surfactant concentration differed for the two types of polymerization systems. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2304–2312, 2006

**Key words:** styrene–butadiene; miniemulsion; copolymerization; polymer kinetics; calorimetry

## INTRODUCTION

As one of the most important polymers with wide application, copolymers of styrene and butadiene are generally synthesized using conventional emulsion polymerization methods.<sup>1</sup> Because of the behavior of butadiene monomer and the characteristics of the emulsion polymerization process, in which nucleation takes place mainly in micelles, the final conversion in copolymerizations of styrene and butadiene via conventional emulsion polymerization is usually limited to relatively low levels (e.g., about 60% for SBR rubbers) to avoid a large amount of gel formation (insoluble polymer), which is adverse to the processibility of SBR rubber.

Gel formation occurs because of the two carbon–carbon double bonds in the butadiene monomer, whereby additions may be of three varieties, *cis*-1,4, *trans*-1,4, or vinyl, and the remaining double bonds after propagation are still reactive. Compared with the double bonds formed in the 1,4-addition reaction, the ones present in the vinyl-addition reaction are more

reactive. These vinyl-addition double bonds may continue to react to form branches or crosslinked structures. Therefore, when the ratio of the crosslinking rate coefficient to the propagation rate coefficient increases, or when the ratio of monomer-to-polymer in the particles decreases below a critical point, the degree of crosslinking increases rapidly, resulting in gel formation. Based on these considerations, several methods are often used to reduce the extent of gel formation: (1) the polymerization is carried out at a low temperature (e.g., 5°C) to decrease the crosslinking rate coefficient of the reaction,<sup>2</sup> or (2) a chain transfer agent is added to decrease the molecular weight and extent of branching.<sup>3</sup> In this study, another possible approach is investigated by performing the copolymerization via the miniemulsion method.

A miniemulsion consists of relatively stable submicron (50–500 nm) dispersions of oil droplets in water usually prepared by shearing a system containing oil, water, surfactant, and additionally, a costabilizer.<sup>4</sup> A miniemulsion polymerization is generally considered to differ from a conventional emulsion polymerization in terms of the nucleation mechanism, as well as the properties of the resulting latexes. A number of research efforts have shown the differences between these two kinds of polymerizations.<sup>5–7</sup> In a miniemulsion polymerization, nucleation typically takes place in the small and relatively stable monomer droplets,

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instead of in monomer-swollen micelles as in the case of conventional emulsion polymerization. The particles created from the miniemulsion monomer droplets are larger in size and relatively rich in monomer during the early stages of the polymerization, as compared with the newly nucleated particles in a conventional emulsion polymerization. Therefore, it is expected that this increase in the ratio between the monomer and polymer within the particles would reduce the levels of branching and delay the formation of gel to higher conversions. This is the reason for investigating miniemulsion polymerization as a means of preparing poly(styrene-*co*-butadiene) latices.

Since butadiene monomer is in a gaseous state at STP conditions, it is not as easy to handle as other monomers, particularly in carrying out the usual miniemulsification process. Therefore, in this study, a modified two-step homogenization procedure was developed and used for the copolymerization of styrene and butadiene monomers via miniemulsion using the Mettler RC1 calorimeter reactor and a 1-L medium pressure reactor (MP10).

## EXPERIMENTAL

### Materials

The chemicals used in this work include styrene (Sigma-Aldrich, St. Louis, MO), butadiene (Air Products and Chemicals, Allentown, PA), hexadecane (HD; Fisher Scientific, Springfield, NJ), sodium lauryl sulfate (SLS; Fisher), and potassium persulfate (KPS; Sigma-Aldrich). The styrene monomer was treated by passing it through an inhibitor-removal column (Sigma-Aldrich) before use. The butadiene monomer was first cleaned by passing it through two successive columns to remove the moisture (Drierite, Fisher) and the inhibitor (Ascarite II; Thomas Scientific, Swedesboro, NJ). It was condensed using a bath comprising a mixture of liquid nitrogen and isopropanol and then charged into a 300-mL stainless steel cylinder. All other chemicals were used as received. Deionized water was used in all polymerizations.

### Miniemulsion preparation

Styrene miniemulsions with HD as costabilizer were prepared in the following way. The surfactant, SLS, was dissolved in the deionized water and the monomer was mixed with the HD. The latter was then added to the aqueous solution and the resulting mixture was homogenized by first sonifying for 60 s at 50% duty, power 7 (Branson sonifier model 450, Ultrasonics, Danbury, CT) to create a crude emulsion, which was subsequently passed through the Microfluidizer (Model 110T, Microfluidics Corp., Newton, MA)

**TABLE I**  
Basic Recipe for the Emulsion and Miniemulsion Copolymerization of Styrene and Butadiene at 70°C

Ingredient	Amount	Weight (g)
Deionized water	80 parts	480.0
Sodium lauryl sulfate	10 mM <sup>a</sup>	1.3834
Hexadecane	0 or 30 mM <sup>b</sup>	0 or 3.260
Potassium persulfate	1.33 mM <sup>a</sup>	0.1726
Sodium bicarbonate	1.33 mM <sup>a</sup>	0.0537
Styrene/butadiene (70 : 30 weight ratio)	20 parts	120.0

<sup>a</sup>Based on aqueous phase.

<sup>b</sup>30 mM based on aqueous phase (2.7 wt % based on monomer) for miniemulsion polymerizations.

10 times with a pump inlet pressure set point of 80 psig. After homogenization, all of the styrene miniemulsions appeared homogeneous and opaque. The styrene/butadiene miniemulsions were then created by adding the butadiene monomer to the styrene miniemulsions with mixing (400 rpm, pitched blade impeller with baffle) and under pressure, allowing 20 min for the butadiene to be absorbed by the styrene miniemulsion droplets. This was accomplished in the MP10 reactor as described below.

### Polymerization

The basic recipe used in this study is presented in Table I. Each polymerization was carried out at 70°C using the RC1 (Mettler-Toledo, Columbia, MD). For a conventional emulsion copolymerization, the surfactant and water solution was first charged into the MP10 reactor, and the reactor was purged with nitrogen for about 10 min, and then, the pressure cylinder containing the butadiene monomer was connected to the reactor via quick disconnect fittings. Before charging the butadiene monomer, any possible leaks were carefully checked using a soap solution. Then, the temperature of the reactor was decreased to about 15°C, and the butadiene monomer was charged into the reactor.

After the addition of butadiene monomer, the system was slowly heated to the reaction temperature and then held there for about 40 min while the calorimeter was calibrated. An aqueous initiator solution (KPS) was then injected to begin the polymerization. During the reaction, the jacket and fluid temperatures, and the pressure within the reactor were recorded automatically by the RC1. The evaluation software was used to obtain the heat of reaction ( $Q_r$ ) profile.

The procedure for the miniemulsion polymerizations was similar to the preceding except for the modifications as mentioned earlier.

## Characterization

Samples for various analyses were periodically withdrawn from the reactor using a syringe (~2 mL). These were short-stopped immediately with an 1% aqueous hydroquinone solution and placed in an ice bath.

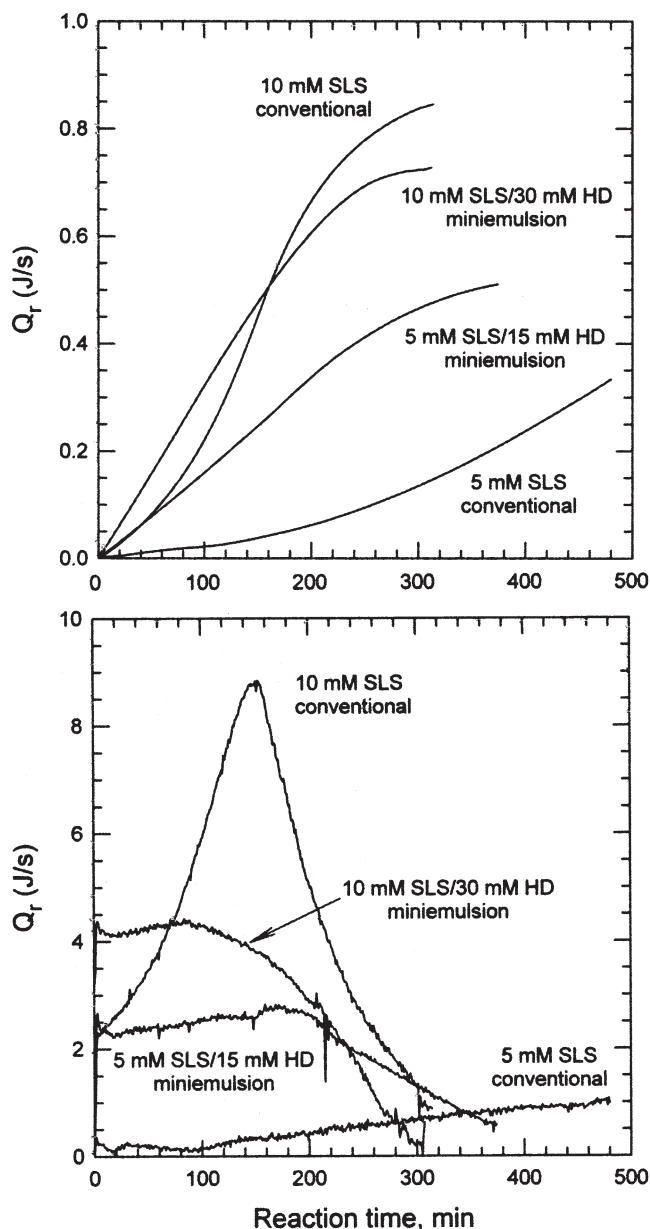
The characteristics of the poly(styrene-*co*-butadiene) latexes were determined using several techniques. Particle size and distributions were obtained by capillary hydrodynamic fractionation (CHDF-1100, Matec Applied Sciences, Northborough, MA). The fractional calorimetric conversion was monitored using the RC1 data. Gravimetry was used to determine the final gravimetric conversion. The amount of unreacted styrene monomer was measured via gas chromatography using dioxane as the internal standard and based on a calibration curve. The butadiene composition in the copolymer was estimated by subtracting the reacted styrene fraction from the overall conversion. The kinetics of the polymerization were then analyzed based on the RC1 data.

## RESULTS AND DISCUSSION

### Conventional emulsion versus miniemulsion copolymerization

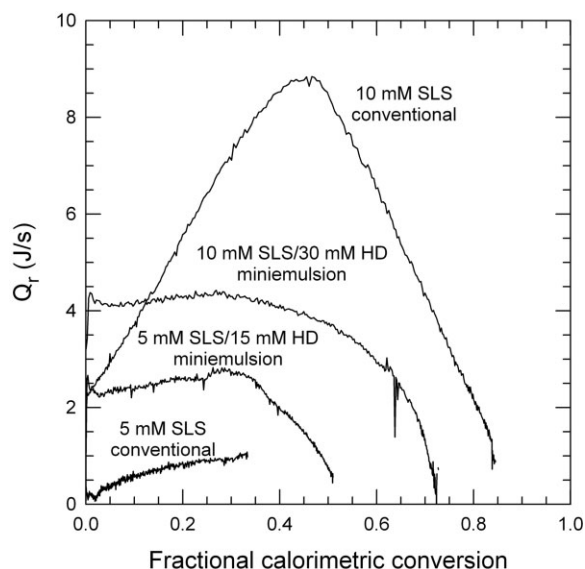
It is generally accepted that nucleation in conventional emulsion polymerizations occurs mainly in monomer-swollen micelles although homogeneous nucleation can also occur to a significant extent.<sup>8,9</sup> Water-soluble initiator decomposes forming free radicals, which propagate in the aqueous phase until they become surface active and then enter micelles to generate latex particles (micellar nucleation) or propagate further in the aqueous phase, precipitating to form particles (homogeneous nucleation). The kinetics of emulsion polymerization were first described by the Smith-Ewart theory.<sup>10</sup> On the other hand, the primary nucleation sites in a miniemulsion polymerization are the small monomer droplets causing the kinetics of polymerization to differ from similar conventional emulsion polymerizations.

Figure 1 shows the conversion (top) and corresponding heat of reaction (bottom) versus time curves for conventional and miniemulsion copolymerizations of 70/30 (wt/wt) styrene/butadiene carried out both above (10 mM SLS) and below (5 mM SLS) the critical micelle concentration (cmc) of the surfactant (7.7 mM). The miniemulsions employed 30 mM HD (2.7 wt % on monomer) and 15 mM HD (1.4 wt % on monomer) for the 10 and 5 mM SLS systems, respectively. The kinetics are striking in their similarities and differences. First, the two conventional polymerizations differ considerably. The reaction carried out below the cmc is slow and only reaches a conversion of 35% after almost 500 min of polymerization at 70°C. In contrast,



**Figure 1** Conversion (top) and heat of reaction ( $Q_r$ ) (bottom) versus reaction time for the conventional emulsion and miniemulsion copolymerizations of 70 : 30 weight ratio styrene/butadiene with surfactant concentrations below (SLS = 5 mM) and above (SLS = 10 mM) the cmc;  $T_r$  = 70°C, [KPS] = 1.33 mM, 400 rpm.

with 10 mM SLS, the reaction rate increases rapidly in the first few minutes after addition of the initiator, as reflected in a heat of reaction of 2.3 J/s. It then increases more slowly to a maximum (8.8 J/s) after about 150 min reaction, this corresponding to about 45% conversion (calorimetric conversion), as shown in Figure 2, and then decreases steadily. These two increases in the rate are taken to indicate regions dominated by micellar and homogeneous nucleation, respectively. This conclusion is based on the work of



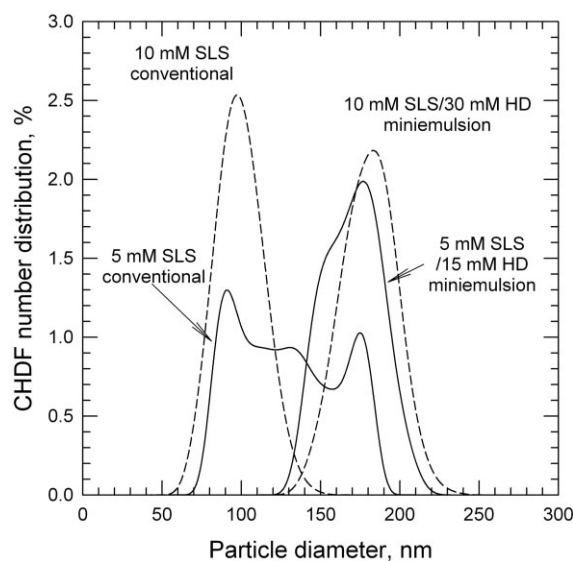
**Figure 2** Heat of reaction ( $Q_r$ ) versus calorimetric conversion for the conventional emulsion and miniemulsion copolymerizations of 70 : 30 weight ratio styrene/butadiene corresponding to the data in Figure 1.

Varela de la Rosa et al., who demonstrated in the conventional emulsion polymerization of styrene that homogeneous nucleation played a major role in polymerizations starting with surfactant concentrations well above the cmc.<sup>8,9</sup> The rate maximum is considered to correspond to the disappearance of monomer droplets.

The two miniemulsion polymerizations, in contrast, are more similar in appearance. The rates ( $Q_r$ ) increase rapidly upon addition of the KPS solution and reach a maximum followed by a small decrease. This is followed by a modest increase in  $Q_r$  to maxima at about 27% conversion in both reactions, followed by a decrease. Qualitatively similar results were recently reported by Anderson et al.<sup>11</sup> for the miniemulsion homopolymerization of styrene, although that system differed in the reaction temperature (50°C) and initiator system (redox). The initial increase in the rates differ substantially where the system with twice the concentrations of stabilizers (10 mM/30 mM = SLS/HD) is about 63% faster than at the lower concentrations (5 mM/15 mM = SLS/HD). This is not surprising considering that droplet nucleation is considered to dominate these reactions. The increased concentrations of both the anionic surfactant, SLS, and the costabilizer, HD, lead to more droplets, which are also expected to be more stable against both collisional and diffusional (Ostwald ripening) degradation. Rapid droplet nucleation is considered responsible for the initial kinetics. Without detailed information regarding the evolution of the number of particles, we can only speculate based on other systems what is occurring in the remainder of the reactions. The slight de-

crease in rate early on could be an evidence of some limited aggregation (reducing the number of particles,  $N_p$ ), while the modest increase in the rate generally indicates an increasing  $N_p$ , which could be brought about by some homogeneous nucleation. However, the rate might also increase because of the preferential consumption of butadiene monomer, which has a reactivity ratio favoring its incorporation with a low propagation rate constant ( $r_{Bu} = 1.39$ ,  $r_S = 0.78$  at 60°C<sup>12</sup>;  $k_p$  (Bu) = 132 dm<sup>3</sup>/(mol s),<sup>13</sup>  $k_p$  (S) = 326 dm<sup>3</sup>/mol s at 70°C<sup>7</sup>). More puzzling are the conversions achieved in these reactions. A lower rate resulted in a lower final conversion (Fig. 2). The cause for this is not known.

Additional information regarding these reactions is given in Figure 3 and Table II. The former presents the final particle size number distributions (PSD) as obtained by CHDF. The smaller particles (greater  $N_p$ ) produced in the conventional emulsion copolymerization carried out above the cmc are expected and correlate with the faster kinetics. The corresponding particles produced below the cmc are multimodal in PSD, indicating that limited aggregation as well as a lengthy nucleation was likely in this reaction. The PSDs for the miniemulsions are not as consistent. Significantly smaller particles were expected at the higher stabilizer level. Although more particles were produced (Table II), the difference is not great. The PSD for the lower stabilizer level has a shoulder indicating a bimodal distribution, while none appears at the higher level. This might indicate a mixed nucleation mechanism (i.e., droplet and homogeneous), although no supporting evidence is given by the kinetics.



**Figure 3** CHDF particle size distributions of the final latex particles resulting from the conventional emulsion and miniemulsion copolymerizations of 70 : 30 weight ratio styrene/butadiene corresponding to the reactions in Figures 1 and 2.

TABLE II  
Kinetic Details Obtained for Styrene/Butadiene Copolymerizations Using Different Polymerization Methods

Method	$Q_r$ max (J/s)	X at $Q_r$ max (%)	Time at $Q_r$ max (min)	Final X (%)	Time at final X (min)	Final $N_p$ ( $\times 10^{-17}$ dm <sup>3</sup> )
Conventional						
Below cmc <sup>a</sup>	–	–	–	35	480	~0.3
Above cmc	8.84	47	153	56	314	3.5
Miniemulsion						
Below cmc	2.83	26	158	72	374	0.43
Above cmc	4.42	27	84	85	312	0.47

<sup>a</sup>After 8 h reaction, the maximum was not reached.

Comparison of the miniemulsion polymerization with the conventional emulsion polymerization reveals significant differences. Initially, both miniemulsion polymerizations are substantially faster than their conventional counterparts. Droplet nucleation leads to significantly faster rates of reaction; more particles are nucleated with the addition of initiator and these contain a high concentration of monomer (as dictated by the thermodynamics). Nucleation either ends or slows substantially in the miniemulsion polymerizations, while it continues by homogeneous nucleation in the conventional reactions.

#### Role of homogenization process

A stable miniemulsion system can be obtained by use of a costabilizer (low molecular weight and low water-solubility) and an instrument providing high shear. The effect of these factors was studied in more detail. First, the effect of the homogenization process on the conventional emulsion system was investigated by using the Microfluidizer to first "homogenize" the styrene monomer (no HD costabilizer), followed by the addition of the butadiene monomer. The kinetics results are shown in Figure 4. No difference is evident with or without homogenization indicating, that the nucleation mechanisms were the same (micellar and homogeneous). Obviously, the droplets created by the shear were not thermodynamically stable, degrading to large size droplets in the time frame required to prepare the material for polymerization in the RC1 (~2 h). It should be noted that these results differ from that reported by Tang et al.<sup>14</sup> In that work, droplet nucleation was inferred in styrene homogenized emulsions from a decreased polymerization rate with increasing aging (degradation) as affected by time and temperature. This could be related to the differing system and procedures used. In our study, the two-step method was used to add the monomers. The styrene emulsion was prepared using the Microfluidizer, and then, the butadiene was added to be absorbed into the already existing styrene monomer droplets. Therefore, the added butadiene monomer may affect the limited stability of the styrene emulsion

system. When the butadiene (30% by weight and 39% by volume at 25°C, both based on total monomer) was added to the system, it could diffuse into the styrene monomer droplets or the styrene monomer could diffuse from the styrene droplets to the larger butadiene droplets. Actually, both should be expected. Since the styrene monomer droplets formed using the Microfluidizer without costabilizer are thermodynamically unstable, the styrene monomer would readily diffuse to the butadiene monomer droplets, leading to monomer droplets in equilibrium with monomer-swollen micelles. In the styrene homopolymerization case of Tang et al., there was no second addition of monomer; the homogenized emulsion system could have some limited stability on the time scale of the experiment, and consequently, there could be nucleation in the monomer droplets, resulting in the different reaction kinetics.

The kinetics data listed in Table III also support the mechanism of nucleation. The maximum heats of re-

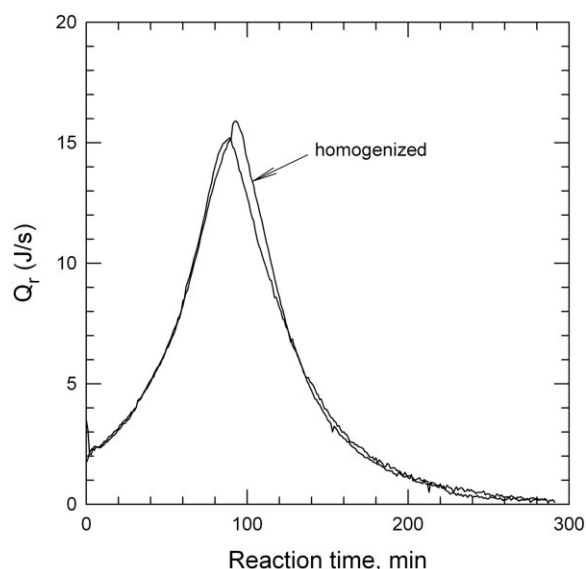


Figure 4 Heat of reaction ( $Q_r$ ) versus reaction time for the conventional emulsion polymerization of 70 : 30 weight ratio styrene/butadiene with and without the styrene prehomogenization process;  $T_r = 70^\circ\text{C}$ ,  $[\text{KPS}] = 10$  mM,  $[\text{SLS}] = 10$  mM, 400 rpm.

TABLE III  
Kinetics Data for Conventional Emulsion Copolymerizations of 70 : 30 Weight Ratio Styrene/Butadiene With and Without Homogenization of the Styrene Monomer

Method	$Q_r$ max (J/s)	$X$ at $Q_r$ max (%)	Time at $Q_r$ max (min)	$D_v$ (nm)	Final $X$ (%)	Final $N_p$ ( $\times 10^{-17}$ /dm <sup>3</sup> )
Without homogenization	15.90	48	93	83	95	7.8
With homogenization	15.21	44	89	89	93	6.2

action were almost the same, and the fractional conversions at these maxima were close. All of these indicate that the monomer droplets were not a primary source of nucleation in this system despite use of the high-shear Microfluidizer.

### Role of HD

The role of the costabilizer (HD) in the miniemulsion system is critical. It allows the system of submicron-size monomer droplets to be sufficiently stable such that these can serve as the main locus of particle nucleation. Compared with another commonly used costabilizer cetyl alcohol (CA), HD acts to stabilize the miniemulsion system by its low molecular weight and low water solubility (the solubilities of CA and HD in water are  $10^{-5}$  and  $10^{-6}$  g/dm<sup>3</sup>, respectively<sup>7</sup>), and its presence inside the monomer droplets. This reduces the diffusion of monomer from the smaller to the larger monomer droplets (Ostwald ripening) and results in a relatively long stability of the miniemulsion system. By using CA as costabilizer, the surface of the monomer droplets is covered by a "condensed phase" of the surfactant and costabilizer in addition to the CA present inside the droplets. These act to reduce the droplet degradation, consequently, making the miniemulsion system stable, although less so than HD systems.

The effect on the reaction kinetics of simply adding HD to the monomer (2.7 wt % on total monomer) without application of the high shear forces of the Microfluidizer was investigated as a control experiment. The HD was dissolved in the styrene monomer and then charged into the reactor, followed by the butadiene as in the other conventional emulsion copolymerizations. The results are shown in Figure 5. It can be seen that the addition of HD to the conventional emulsion system did affect the reaction kinetics; the overall rate of polymerization became slower when HD was added, although the basic shape of the curve remained the same. This was not expected. In fact, no significant effect was expected. However, based on these results and those reported in Table IV, some speculation can be offered. Although the shear in the MP10 reactor (400 rpm, pitched blade impeller with baffle) is considered minimal compared with the Microfluidizer, in fact, smaller droplets (micron size) sta-

bilized against diffusive degradation by the presence of HD could be produced, which have an average size substantially smaller than in the counterpart system without HD. These droplets would adsorb more of the surfactant (SLS) and thus reduce the number of micelles initially available for nucleation. This would explain the lowered initial rate of polymerization upon addition of the KPS. In addition, the presence of HD in the monomer droplets could affect the adsorption behavior of the SLS on their surfaces, increasing the hydrophobicity and thus reduce the aqueous phase-free SLS. This was recently reported by Erdem et al.,<sup>15</sup> where the saturation area of SLS on styrene/HD mixtures (3.5 wt % HD on styrene) was 71.2 Å<sup>2</sup> per molecule as compared with 76.7 Å<sup>2</sup> per molecule on styrene monomer alone. This would effectively reduce the amount of surfactant available to stabilize particles, thus reducing the number nucleated either by micellar or homogeneous nucleation.

An additional possibility is that the presence of HD in the droplets could also affect the distribution of the monomers between the particles and the droplets

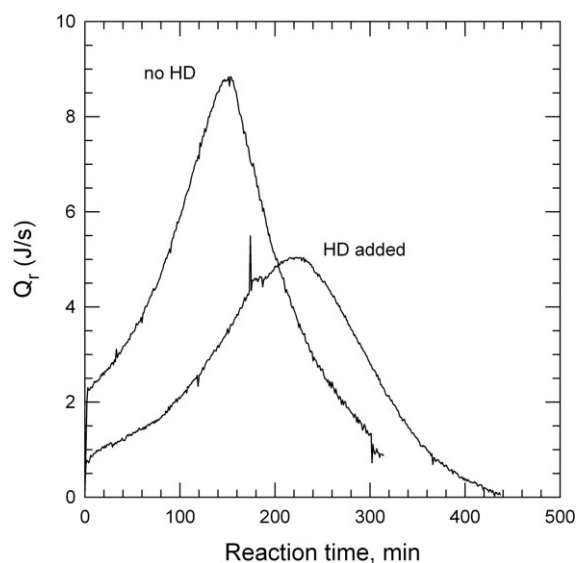


Figure 5 Heat of reaction ( $Q_r$ ) versus reaction time for the conventional emulsion polymerization of 70 : 30 weight ratio styrene/butadiene with and without adding 30 mM hexadecane;  $T_r = 70^\circ\text{C}$ ,  $[\text{KPS}] = 1.33 \text{ mM}$ ,  $[\text{SLS}] = 10 \text{ mM}$ , 400 rpm.

TABLE IV  
Kinetics Data for Conventional Emulsion Copolymerizations of 70 : 30 Weight Ratio Styrene/Butadiene With and Without Addition of HD

Method	$Q_r$ max (J/s)	$X$ at $Q_r$ max (%)	Time at $Q_r$ max (min)	$D_v$ (nm)	Final $X$ (%)	Final $N_p$ ( $\times 10^{-17}/\text{dm}^3$ )
Without HD	8.84	47	153	98	85	4.2
With HD	5.04	47	222	105	84	3.4

shifting the equilibrium toward the droplets, thereby reducing the concentrations in the particles and contributing to a lower rate of polymerization. Without further study, however, these remain speculation.

### Effect of SLS concentration

#### Conventional emulsion copolymerization

It was clear from the beginning that the emulsifier concentration plays an important role in emulsion polymerization. Based on the classical Smith–Ewart theory,<sup>10</sup> the rate of polymerization is dependent on the emulsifier concentration to the 0.6 power. By increasing the emulsifier concentration, more micelles are formed and thus more particles are nucleated, resulting in faster rates of polymerization. In mini-emulsion polymerizations, the situation is similar in that more emulsifier allows more droplets to be stabilized and subsequently nucleated to form particles.

Figure 6 presents the kinetics results for the conventional emulsion copolymerization of styrene and butadiene at four levels of SLS: 5, 10, 20, and 30 mM. The overall rate of polymerization increased with the surfactant concentration, as expected. For the reaction with the surfactant concentration below the cmc, the rate of polymerization was quite slow, as shown previously. Above the cmc, some similar behaviors were observed. First, each curve shows a rapid rise in the rate followed by a more moderate rise, as seen earlier. This rapid rise ends at increasingly higher rates with increasing surfactant. As indicated previously, the initial rise is attributed to particle nucleation in micelles and is expected to be proportional to the number of micelles initially present in the system. This is roughly the case here. The initial rate increased 2.2 times for a doubling of the surfactant concentration and 3.6 times for a tripling. The rate increase, in what we refer to as Stage 2,<sup>9</sup> is roughly the same for each reaction ( $\sim 7 \pm 0.4$  J/s), indicating that similar extents of homogeneous nucleation are considered to occur in each polymerization. All proceed to a rate maximum at about the same conversion of  $44\% \pm 2\%$ , where monomer droplets disappear.

The final particle size (volume-average; CHDF) and estimated number of particles for each reaction are given in Table V. The rate ( $Q_r$  max) increased with increasing  $N_p$ , however not proportionately. Going

from 10 to 30 mM SLS resulted in a 100% increase in  $N_p$  and only a 77% increase in the rate. This is likely the result of the small particle size produced in the latter reaction ( $D_v = 80$  nm). In this case,  $\bar{n}$ , the average number of radicals per particle, would likely drop below  $\frac{1}{2}$  as caused by increased radical desorption. Further analysis shows that  $Q_r$  max is proportional to the 0.52 power of the surfactant concentration, while the  $N_p$  dependency is 0.63. The latter is close to the classical Smith–Ewart prediction of 0.6, indicating a strong similarity to the homopolymerization of styrene. This result is not the same as that reported for the homopolymerization of butadiene. Weerts<sup>16</sup> found that the polymerization of butadiene via conventional emulsion polymerization showed dependencies of  $R_p$  and  $N_p$  on the surfactant (SLS) concentration to the 0.24 and 2.1 powers, respectively. The author attributed these results to limited aggregation occurring to varying extents during the polymerizations. In our study, however, only 30 wt % of the monomer is butadiene.

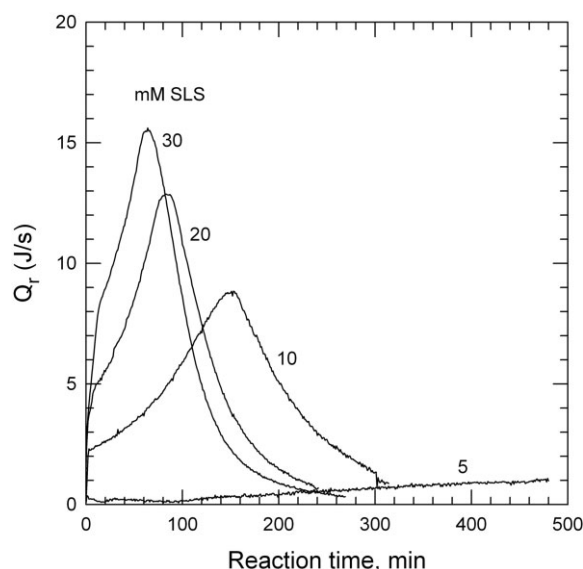


Figure 6 Heat of reaction ( $Q_r$ ) versus reaction time for the conventional emulsion copolymerizations of 70 : 30 weight ratio styrene/butadiene indicating the effect of surfactant (SLS) concentration; [KPS] = 1.33 mM,  $T_r = 70^\circ\text{C}$ , 400 rpm.

TABLE V  
Kinetics Data for Conventional Emulsion Copolymerizations of 70 : 30 Weight Ratio Styrene/Butadiene with Different Surfactant Concentrations

[SLS] (mM)	$Q_r$ max (J/s)	X at $Q_r$ max (%)	Time at $Q_r$ max (min)	$D_v$ (nm)	Final X (%)	Final $N_p$ ( $\times 10^{-17}/\text{dm}^3$ )
10	8.84	47	153	98	85	4.2
20	12.87	39	83	85	82	6.3
30	15.62	42	64	80	92	8.5

### Miniemulsion copolymerization

Parallel results for the miniemulsion copolymerizations are shown in Figure 7 using HD as costabilizer and held at a fixed ratio of SLS to HD of 1 : 3. This formulation strategy deserves some comment. In fact, it is a holdover from prior work using SLS and CA as the surfactant/costabilizer combination. Styrene miniemulsion stability was found to be optimum at a mole ratio of about one SLS to three CA.<sup>17</sup> These results influenced the work with HD as costabilizer despite the fact that no association of SLS and HD was expected, with HD distributed inside the monomer droplets rather than partly at the interface. Nonetheless, this is the origin of this methodology and why the ratio is presented for both ingredients based on the aqueous phase.

The results in Figure 6 show that there are some superficial similarities to the corresponding conventional emulsion polymerizations. The overall rate of polymerization increased with the surfactant/costabilizer concentration, indicating more droplets were formed and nucleated. The differences are more notable, however. First, the shapes of the curves are

strikingly different from the conventional reactions. This was indicated in Figure 1, but is now even more apparent. At the 20 mM/60 mM stabilizer/costabilizer levels, the initial rate is increased substantially (i.e.,  $Q_r$  increases 140% for a 100% increase in the stabilizer level from 10 mM/30 mM to 20 mM/60 mM SLS/HD). The further increase in the stabilizer levels also leads to an increase in  $Q_r$ , but not to such a large extent. Both curves show a decrease in  $Q_r$  followed by a leveling off at a near constant rate followed by a decrease as monomer is consumed in the particles (i.e., decreasing monomer concentration). These differ from the two lower levels of stabilizer/costabilizer, which showed a modest increase in  $Q_r$  before decreasing. Although the cause of the initial rate maximum is not clear, since we have no supporting data in these early minutes of the reaction, some possibilities can be described. Earlier, it was stated that limited aggregation (decreasing  $N_p$ ) might account for such a behavior. But, why this should happen is not obvious. Two other possibilities exist. The monomer concentration could drop in the particles as a result of the changing thermodynamics resulting from polymer formation, but this would require that it goes somewhere (i.e., nonnucleated droplets). This does not seem likely. The third possibility is a reduction in  $\bar{n}$ . If rapid nucleation of droplets occurs in the first few seconds of the reaction, then conceivably,  $\bar{n}$  could initially be close to unity. By further polymerization with radical entry, exit, and termination occurring, a pseudo steady-state value below one would certainly result, thus causing the reduction in the rate. No one has ever reported such a behavior, however. So, it is not clear that if any of these can explain this observed and reproducible phenomenon.

Additional data are reported in Table VI. The large increase in  $Q_r$  noted above correlates with a large decrease in the particle size (increased  $N_p$ ). This decrease is a direct result of a decreased droplet size brought about not only by the additional SLS but also the increased stability against diffusional degradation (Ostwald ripening) with the higher concentration of HD within the droplets (5.4 wt % on monomer). It should be noted that the surface area of the resulting particles increased  $\sim 1.9\times$  with a

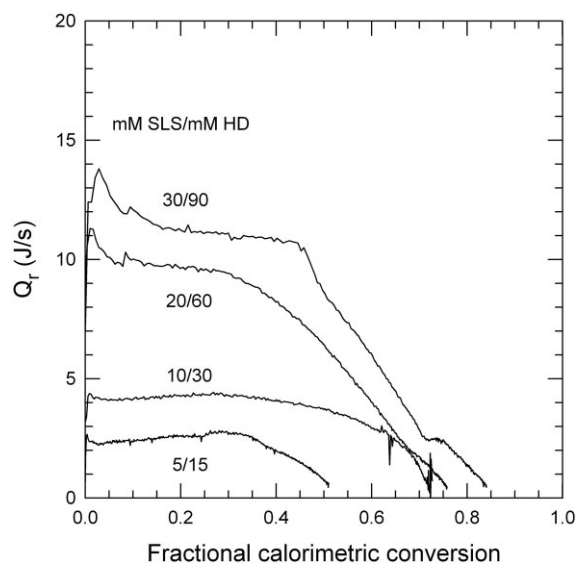


Figure 7 Heat of reaction ( $Q_r$ ) versus reaction time for the miniemulsion copolymerizations of 70 : 30 weight ratio styrene/butadiene indicating the effect of SLS/HD concentrations;  $T_r = 70^\circ\text{C}$ ,  $[\text{KPS}] = 1.33 \text{ mM}$ , 400 rpm.



TABLE VI  
Kinetics Data for Miniemulsion Copolymerizations of 70 : 30 Weight Ratio Styrene/Butadiene with Different Surfactant/Costabilizer Concentrations

[SLS]/[HD] (mM)	$Q_r$ max (J/s)	X at $Q_r$ max (%)	Time at $Q_r$ max (min)	$D_v$ (nm)	Final X (%)	Final $N_p$ ( $\times 10^{-17}/\text{dm}^3$ )
5/15	2.83	26	158	177	51	0.43
10/30	4.42	27	84	183	73	0.56
20/60	11.30	1	2	103	76	3.3
30/90	13.80	3	4	89	84	5.6

doubling of the stabilizer/costabilizer levels. This is not typical in emulsion polymerization or miniemulsion polymerization. The dependencies of  $Q_r$  max and  $N_p$  on the surfactant (SLS) concentration were determined to be 1.1 and 2.2, respectively, representing strikingly different values from those reported for the conventional emulsion polymerizations. The role of the increasing HD is not accounted for here and indeed should play some role in creating such a high dependence of  $N_p$  on the SLS concentration.

## SUMMARY

Miniemulsion and parallel conventional emulsion copolymerizations of styrene and butadiene (70 : 30 wt ratio) were carried out in the RC1 reaction calorimeter at 70°C to gain a further understanding of their reaction mechanisms. The miniemulsions were prepared by first creating a styrene miniemulsion using SLS and HD as surfactant and costabilizer, followed by charging neat butadiene into the reactor and allowing sufficient time for its absorption into the miniemulsion droplets. The polymerizations were carried out by the addition of KPS. Droplet nucleation was inferred from the substantial differences in the reaction kinetics and particle size of those produced from the miniemulsions and conventional emulsions. The latter was considered to proceed by both micellar and homogeneous nucleation.

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